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Acta Cryst. (1993). **C49**, 1363–1365

Structure of Dicarbonylbis-(μ -3,5-dimethylpyrazolyl)-bis(4-tolyl diphenylphosphinite)diiridium(I)-Dichloromethane (1/1)

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(Received 18 June 1992; accepted 9 December 1992)

Abstract

In bis(μ -3,5-dimethylpyrazolyl-*N,N'*)-bis[carbonyl(4-tolyl diphenylphosphinite-*P*)iridium(I)] dichloromethane solvate, two Ir^I atoms are joined by two 3,5-dimethylpyrazolyl bridges with one carbonyl and one 4-tolyl diphenylphosphinite ligand completing the square-planar geometry about each Ir atom. The Ir...Ir distance of 3.307 (1) Å is greater than the distance of 3.22 Å found in a similar pyrazolyl-bridged iridium(I) dimer [Fox (1989). PhD dissertation, California Institute of Technology, USA].

Comment

The title compound [Ir(μ -pz*)(CO)(Ph₂POC₆H₄CH₃)]₂, where pz* is 3,5-dimethylpyrazolyl, was synthesized as a model complex for the study of electron transfer in iridium dimer/pyridinium donor-acceptor complexes (Ir₂-

py*). The photophysical and electrochemical data for this compound reveal energetic and kinetic parameters [$E_{00}(S_1) = 2.4$, $E_{00}(T_1) = 1.9$ eV, $E_{1/2}(\text{Ir}_2/\text{Ir}_2^+) = 0.4$ V versus SSCE (sodium saturated calomel electrode), $\tau_S = 125$ ps, $\tau_T = 1$ μ s] used in analyzing electron-transfer rates for the series of Ir₂-py* complexes. The synthesis of this compound is reported elsewhere (Farid, Chang, Winkler & Gray, 1993). Slow evaporation of a methylene chloride/acetonitrile solution produced acicular crystals.

The molecule exhibits approximate *C*_{2v} symmetry. The square-planar Ir atoms are almost identical and are coordinated to two adjacent dimethylpyrazolyl ligands with an average Ir—N distance of 2.077 [10] Å, where square brackets indicate a scatter e.s.d. A carbonyl ligand at 1.804 [9] Å and a tolyl diphenylphosphinite group with an Ir—P bond of 2.224 [0] Å complete the coordination shell about each Ir atom. The N—Ir—N angle is 84.1 [14]° and the other three angles about the Ir atom range from 91.4 [6] to 92.4 [4]°.

The bridging pyrazolyl groups retain the structure of the free ligand. The dihedral angle between the two pyrazolyl groups is 78.8 (6)°. The torsion angles Ir(1)—N(1)—N(2)—Ir(2) and Ir(1)—N(3)—N(4)—Ir(2)

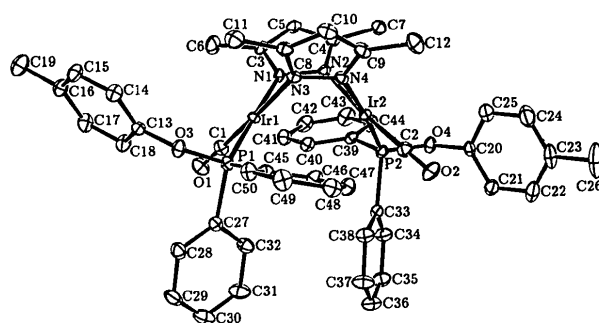


Fig. 1. An ORTEP view of the dimer with 15% probability ellipsoids. H atoms are not shown.

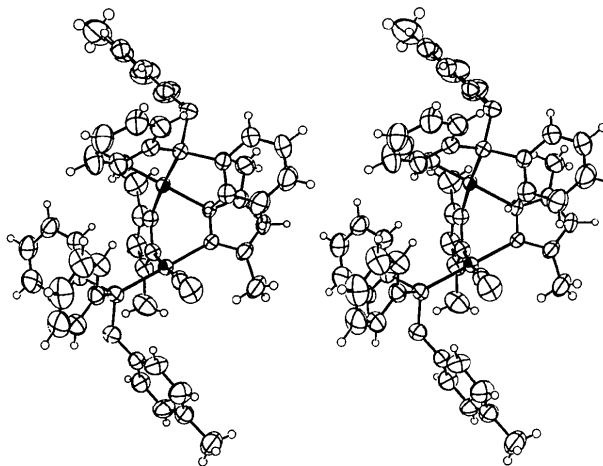


Fig. 2. An ORTEP stereoview of the iridium complex; atoms are drawn at the 50% probability level with H atoms at one tenth scale.

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are 12.1 (4) and 4.9 (4)°, respectively. The remaining ligand geometry is as expected. Substantial overlap of the aromatic rings occurs between neighboring molecules in the crystal. The population of the dichloromethane solvate refined to near unity [0.959 (4)].

The Ir...Ir solid-state non-bonding separation of 3.307 (1) Å is similar to the $M \cdots M$ separations in analogous bispyrazolyl-bridged Ir and Rh d^8 - d^8 dimers. For six iridium compounds (Nussbaum, Rettig, Storr & Trotter, 1985; Beveridge, Bushnell & Stobart, 1983; Coleman, Eadie, Stobart, Zaworotko & Atwood, 1982; Beveridge, Bushnell, Dixon, Eadie, Stobart, Atwood & Zaworotko, 1982; Fox, 1989), the average Ir...Ir separation is 3.28 [12] Å (ranging from 3.162 to 3.506 Å); and for four rhodium compounds (Beveridge, Bushnell & Stobart, 1983; Louie, Rettig, Storr & Trotter, 1984; Uson, Oro, Ciriano, Pinillos, Tiripicchio & Carmellini, 1981), the average Rh...Rh separation is 3.31 [18] Å (ranging from 3.154 to 3.568 Å).

Experimental

Crystal data

[Ir₂(C₅H₇N₂)₂(C₁₉H₁₇OP)₂-(CO)₂].CH₂Cl₂

$M_r = 1300.28$

Monoclinic

$P2_1/c$

$a = 18.677$ (2) Å

$b = 13.817$ (1) Å

$c = 20.225$ (3) Å

$\beta = 101.37$ (1)°

$V = 5116.8$ (10) Å³

$Z = 4$

$D_x = 1.69$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 24

reflections

$\theta = 15$ – 16.5°

$\mu = 5.391$ mm⁻¹

$T = 293$ K

Irregular

$0.6 \times 0.6 \times 0.4$ mm

Orange-red

Data collection

Enraf-Nonius CAD-4 diffractometer

θ scans

Absorption correction:

by integration from crystal shape

$T_{\min} = 0.39$, $T_{\max} = 0.54$

14173 measured reflections

6662 independent reflections

6662 observed reflections

$\theta_{\max} = 22.5^\circ$

$h = -20 \rightarrow 20$

$k = 0 \rightarrow 14$

$l = -21 \rightarrow 21$

3 standard reflections

frequency: 180 min

intensity variation: 2%

Refinement

Refinement on F^2

Final $R = 0.0316$

$wR = 0.0025$

$S = 1.46$

6662 reflections

588 parameters

H-atom parameters not refined

Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.04$

$\Delta\rho_{\max} = 0.78$ e Å⁻³

$\Delta\rho_{\min} = -0.64$ e Å⁻³

Extinction correction:

Becker-Coppens type 1 isotropic

Extinction coefficient:

0.092 (3) $\times 10^{-6}$

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: CAD-4 software (Schagen, Straver, van Meurs & Williams, 1989). Cell refinement: CAD-4 software. Data reduction: CRYM (Duchamp, 1964). Program(s) used to solve structure: CRYM. Program(s) used to refine structure: CRYM. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: CRYM.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Ir(1)	0.25396 (1)	0.05931 (1)	0.83242 (1)	0.0370 (1)
Ir(2)	0.22477 (1)	0.28327 (2)	0.87831 (1)	0.0384 (5)
P(1)	0.24573 (7)	-0.0576 (1)	0.90619 (1)	0.0438 (3)
P(2)	0.32749 (8)	0.3689 (1)	0.90235 (7)	0.0444 (3)
N(1)	0.2567 (2)	0.1699 (3)	0.7636 (2)	0.041 (1)
N(2)	0.2361 (2)	0.2607 (3)	0.7798 (2)	0.041 (1)
N(3)	0.1458 (2)	0.1024 (3)	0.8281 (2)	0.043 (1)
N(4)	0.1346 (2)	0.1941 (3)	0.8505 (2)	0.044 (1)
O(1)	0.4071 (2)	0.0045 (3)	0.8293 (2)	0.078 (1)
O(2)	0.1901 (3)	0.3201 (3)	1.0135 (2)	0.083 (1)
O(3)	0.2176 (2)	-0.1645 (3)	0.8786 (2)	0.058 (1)
O(4)	0.3235 (2)	0.4862 (2)	0.9104 (2)	0.056 (1)
C(1)	0.3465 (3)	0.0257 (4)	0.8308 (3)	0.055 (2)
C(2)	0.2050 (3)	0.3056 (4)	0.9610 (3)	0.058 (2)
C(3)	0.2700 (3)	0.1753 (4)	0.7005 (3)	0.053 (2)
C(4)	0.2360 (3)	0.3200 (4)	0.7278 (3)	0.052 (2)
C(5)	0.2577 (3)	0.2681 (4)	0.6771 (3)	0.057 (2)
C(6)	0.2934 (4)	0.0880 (5)	0.6668 (3)	0.088 (2)
C(7)	0.2126 (4)	0.4232 (4)	0.7305 (3)	0.073 (2)
C(8)	0.0811 (3)	0.0579 (4)	0.8120 (3)	0.055 (2)
C(9)	0.0631 (3)	0.2048 (5)	0.8470 (3)	0.059 (2)
C(10)	0.0281 (3)	0.1204 (5)	0.8231 (3)	0.070 (2)
C(11)	0.0745 (4)	-0.0424 (5)	0.7848 (4)	0.084 (2)
C(12)	0.0318 (4)	0.2971 (5)	0.8673 (4)	0.090 (2)
C(13)	0.2366 (3)	-0.2126 (4)	0.8231 (3)	0.051 (1)
C(14)	0.1824 (3)	-0.2647 (4)	0.7831 (3)	0.058 (2)
C(15)	0.1987 (3)	-0.3147 (4)	0.7288 (3)	0.066 (2)
C(16)	0.2668 (3)	-0.3135 (4)	0.7135 (3)	0.061 (2)
C(17)	0.3199 (3)	-0.2608 (5)	0.7550 (4)	0.073 (2)
C(18)	0.3057 (3)	-0.2108 (4)	0.8100 (3)	0.062 (2)
C(19)	0.2830 (4)	-0.3656 (5)	0.6525 (4)	0.090 (2)
C(20)	0.2791 (3)	0.5284 (4)	0.9511 (3)	0.052 (2)
C(21)	0.3087 (4)	0.5538 (4)	1.0151 (3)	0.066 (2)
C(22)	0.2653 (5)	0.5975 (5)	1.0548 (4)	0.086 (2)
C(23)	0.1932 (5)	0.6133 (5)	1.0303 (5)	0.090 (3)
C(24)	0.1649 (5)	0.5887 (6)	0.9652 (5)	0.108 (3)
C(25)	0.2078 (4)	0.5465 (5)	0.9249 (4)	0.088 (2)
C(26)	0.1439 (6)	0.6554 (6)	1.0748 (6)	0.162 (4)
C(27)	0.3285 (3)	-0.0854 (4)	0.9670 (3)	0.049 (1)
C(28)	0.3455 (4)	-0.1792 (4)	0.9904 (3)	0.065 (2)
C(29)	0.4075 (4)	-0.1951 (5)	1.0400 (4)	0.083 (2)
C(30)	0.4508 (4)	-0.1209 (7)	1.0666 (4)	0.088 (2)
C(31)	0.4345 (4)	-0.0292 (6)	1.0445 (4)	0.083 (2)
C(32)	0.3739 (3)	-0.0111 (5)	0.9947 (3)	0.065 (2)
C(33)	0.3914 (3)	0.3350 (4)	0.9793 (3)	0.047 (1)
C(34)	0.4586 (3)	0.3813 (5)	0.9961 (3)	0.067 (2)
C(35)	0.5068 (3)	0.3585 (5)	1.0544 (3)	0.075 (2)
C(36)	0.4890 (4)	0.2900 (6)	1.0971 (3)	0.081 (2)
C(37)	0.4232 (4)	0.2420 (6)	1.0807 (3)	0.085 (2)
C(38)	0.3758 (3)	0.2641 (4)	1.0213 (3)	0.064 (2)
C(39)	0.3859 (3)	0.3707 (4)	0.8405 (2)	0.047 (1)
C(40)	0.4139 (3)	0.2828 (4)	0.8237 (3)	0.056 (2)
C(41)	0.4623 (3)	0.2792 (5)	0.7798 (3)	0.069 (2)
C(42)	0.4817 (4)	0.3639 (6)	0.7520 (3)	0.079 (2)
C(43)	0.4531 (4)	0.4502 (5)	0.7673 (4)	0.083 (2)
C(44)	0.4055 (4)	0.4555 (4)	0.8117 (3)	0.069 (2)
C(45)	0.1804 (3)	-0.0385 (4)	0.9609 (3)	0.044 (1)
C(46)	0.1787 (3)	0.0525 (4)	0.9900 (3)	0.060 (2)
C(47)	0.1326 (3)	0.0710 (5)	1.0341 (3)	0.066 (2)
C(48)	0.0882 (3)	-0.0005 (6)	1.0491 (3)	0.070 (2)
C(49)	0.0891 (3)	-0.0890 (5)	1.0210 (4)	0.074 (2)
C(50)	0.1348 (3)	-0.1096 (4)	0.9770 (3)	0.061 (2)

Cl(1)	0.0210 (2)	0.2650 (2)	0.6341 (2)	0.167 (1)
Cl(2)	0.0491 (2)	0.0716 (3)	0.6059 (2)	0.226 (2)
C(51)	0.0790 (5)	0.1722 (7)	0.6512 (5)	0.132 (4)

Table 2. Geometric parameters (Å, °)

Ir(1)—Ir(2)	3.307 (1)	N(3)—N(4)	1.376 (6)
Ir(1)—N(1)	2.075 (4)	N(3)—C(8)	1.337 (7)
Ir(1)—N(3)	2.091 (4)	N(4)—C(9)	1.332 (7)
Ir(2)—N(2)	2.068 (4)	O(1)—C(1)	1.174 (7)
Ir(2)—N(4)	2.073 (4)	O(2)—C(2)	1.165 (7)
Ir(1)—C(1)	1.797 (6)	C(3)—C(5)	1.371 (8)
Ir(2)—C(2)	1.810 (6)	C(3)—C(6)	1.493 (9)
Ir(1)—P(1)	2.224 (1)	C(4)—C(5)	1.377 (8)
Ir(2)—P(2)	2.224 (1)	C(4)—C(7)	1.494 (8)
P(1)—O(3)	1.629 (4)	C(8)—C(10)	1.365 (9)
P(2)—O(4)	1.633 (4)	C(8)—C(11)	1.488 (9)
N(1)—N(2)	1.370 (6)	C(9)—C(10)	1.377 (9)
N(1)—C(3)	1.349 (7)	C(9)—C(12)	1.493 (9)
N(2)—C(4)	1.334 (7)		
P(1)—Ir(1)—N(3)	92.3 (1)	Ir(2)—P(2)—C(39)	117.8 (2)
P(1)—Ir(1)—C(1)	91.0 (2)	Ir(1)—N(1)—N(2)	117.9 (3)
N(1)—Ir(1)—N(3)	85.1 (2)	Ir(1)—N(1)—C(3)	135.1 (3)
N(1)—Ir(1)—C(1)	91.6 (2)	C(3)—N(1)—N(2)	106.8 (4)
P(1)—Ir(1)—N(1)	177.4 (1)	Ir(2)—N(2)—N(1)	117.1 (3)
N(3)—Ir(1)—C(1)	176.3 (2)	Ir(2)—N(2)—C(4)	133.0 (3)
P(2)—Ir(2)—N(2)	92.5 (1)	C(4)—N(2)—N(1)	109.3 (4)
P(2)—Ir(2)—C(2)	91.8 (2)	Ir(1)—N(3)—N(4)	117.2 (3)
N(2)—Ir(2)—N(4)	83.1 (2)	Ir(1)—N(3)—C(8)	134.3 (4)
P(2)—Ir(2)—N(4)	174.2 (1)	C(8)—N(3)—N(4)	108.4 (4)
N(2)—Ir(2)—C(2)	174.1 (2)	C(9)—N(4)—N(3)	107.4 (4)
N(4)—Ir(2)—C(2)	92.9 (2)	Ir(2)—N(4)—N(3)	118.0 (3)
Ir(1)—C(1)—O(1)	179.3 (5)	Ir(2)—N(4)—C(9)	134.5 (4)
Ir(2)—C(2)—O(2)	178.0 (5)	C(5)—C(3)—N(1)	109.2 (5)
Ir(1)—P(1)—O(3)	119.3 (1)	C(5)—C(4)—N(2)	108.2 (5)
Ir(1)—P(1)—C(27)	116.5 (2)	C(4)—C(5)—C(3)	106.5 (5)
Ir(1)—P(1)—C(45)	116.4 (2)	C(10)—C(8)—N(3)	108.6 (5)
Ir(2)—P(2)—O(4)	119.7 (1)	C(10)—C(9)—N(4)	109.1 (5)
Ir(2)—P(2)—C(33)	116.2 (2)	C(9)—C(10)—C(8)	106.5 (5)

Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014\langle I \rangle)^2$. Goodness of fit for merging data was 1.02; R_{merge} for duplicates, 0.020. Dispersion corrections were taken from Cromer & Waber (1974). The final R for $F_o^2 > 3\sigma$ was 0.0235; the final wR , 0.0022. Since the calculated absorption correction increased the goodness of fit for merging, an absorption coefficient corresponding to 30% of the calculated value was used.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55976 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1021]

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Acta Cryst. (1993). **C49**, 1365–1367

Structure of [N,N'-o-Phenylenebis(salicylideneaminato)]iron(III) Chloride as a Five-Coordinate Monomer

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(Received 15 September 1992; accepted 15 January 1993)

Abstract

The crystal contains three independent five-coordinate monomers of chloro-[2,2'-[o-phenylenebis(nitrilomethylidyne)]diphenolato-N,N',O,O']iron(III). The distances Fe(1)—Fe(1A), Fe(1)—Fe(1B) and Fe(1A)—Fe(1B) are 7.175 (1), 7.683 (1) and 7.207 (1) Å, respectively. The planes of the ligand groups of the two neighbouring molecules bend away from each other.

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